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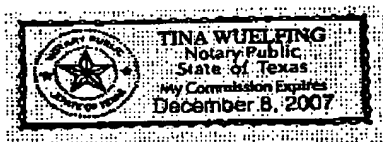
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We certify that the attached English translation conforms essentially to the original German language.

*Kim Vitray*

Kim Vitray  
Operations Manager

Subscribed and sworn to before me this 10th day of August, 2006.



*Tina Wuelfing*

Tina Wuelfing  
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PRIORITY CERTIFICATE CONCERNING THE SUBMISSION OF A PATENT  
APPLICATION

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Applicant/Grantee: Clariant GmbH  
Frankfurt am Main/DE

FUEL OIL WITH IMPROVED LUBRICANT EFFECT CONTAINING MIXTURES OF  
FATTY ACIDS WITH PARAFFIN DISPERSERS, AND A LUBRICANT-IMPROVING  
ADDITIVE.

The attached pages are a true and accurate reproduction of the original documents of this patent application.

Munich, May 23, 2001  
German Patent and Trademark Office  
The President  
By  
[signature]

Fuel oil with improved lubricant effect containing mixtures of fatty acids with paraffin dispersers, and a lubricant-improving additive.

The present invention concerns mixtures of fatty acids and paraffin dispersers with improved low temperature stability and their use for improving the lubricant effect of middle distillate fuel oils.

Mineral oils and mineral oil distillates that are used as fuel oils generally contain 0.5 wt% and more sulfur, which causes the formation of sulfur dioxide upon combustion. To avoid the resulting environmental pollution the sulfur content of fuel oils is continually being reduced. The standard EN 590 that concerns diesel fuels currently prescribes a maximum sulfur content of 350 ppm in Germany. Fuel oils with less than 50 ppm and, in exceptional cases, less than 10 ppm sulfur are already in use in Scandinavia. As a rule, these fuel oils are produced by hydrorefining

the fractions obtained from the petroleum by distillation. However, the desulfurization also removes other substances that give fuel oils a natural lubricant effect. Among these substances are, among others, polyaromatic and polar compounds.

However, it turned out that the friction- and wear-reducing properties of fuel oils are becoming poorer with increasing degrees of desulfurization. Often these properties are so deficient that after only a short time one must expect signs of scoring on the materials lubricated by the fuel, for example the distributor injection pumps of diesel engines. The maximum value for the 95% distillation point, a maximum of 360°C, which has been in effect since the year 2000 per EN 590 the further reduction of the 95% distillation point to under 350°C and in some cases under 330°C that has been undertaken in the meantime in Scandinavia exacerbates this problem even further.

In the prior art therefore there are approaches that are intended to be a solution to this problem (so called lubricity additives).

EP-A-0 798 364 discloses salts and amides of mono- to tetracarboxylic acids with 2 to 50 C atoms and aliphatic mono/polyamines with 2 to 50 c atoms and 1 to 10 N atoms with lubricity additives for low-sulfur diesel fuel. Preferred amines have 8-20 C atoms, for example coco fatty amine, tallow fatty amine and oleylamine.

WO-A-95/33805 discloses the use of low temperature flow improvers to improve the lubricant effect of low sulfur middle distillates. Polar nitrogen-containing compounds that contain an NR<sup>13</sup> group, where R<sup>13</sup> is a hydrocarbon residue with 8 to 40 C atoms and can be in the form of a cation, are also mentioned as suitable substances.

WO-A-96/18706, by analogy with WO-A-95/33805, discloses the use of the nitrogen-containing compounds mentioned there in combination with lubricity additives.

WO-A-96/23855, by analogy with WO-A-95/33805, discloses the use of the nitrogen-containing compounds mentioned there in combination with detergent additives.

The fatty acids used in the prior art have the disadvantage that they solidify when stored at low temperatures, i.e., often at room temperature, mostly at temperatures from 0°C and certainly by -5°C, or crystalline fractions precipitate and cause problems in handling. This problem can only partially be solved by dilution with organic solvents, since fractions crystallize out even from these solutions or the solutions gel and solidify. For use as lubricity additives therefore they have to be highly diluted, or kept in heated storage containers and dispensed via heated lines.

The efficacy of low temperature flow improvers as lubricity additives by themselves is not enough, so that either very high dispensing rates or synergists must be used.

The task underlying the present invention therefore was to find lubricity additives that improved the lubricant effect of middle distillates with low dispensing rates, but themselves remain homogeneous, clear and especially flowable even at low temperatures.

It was found that mixtures of fatty acids with polar nitrogen-containing compounds that are effective as paraffin dispersers in middle distillates remain flowable and clear for a long time even at distinctly lower temperatures, in some cases down to under  $-20^{\circ}\text{C}$ , in particular cases down to  $-30^{\circ}\text{C}$  and in special cases down to  $-40^{\circ}\text{C}$  and, moreover, they improve the lubricant effect of middle distillates more efficiently than do the pure fatty acids of the prior art.

The object of the invention thus consists of low-temperature-stabilized additives for fuel oils with up to 0.05 wt% sulfur content that contain fatty acid mixtures of

A1) 1 to 99 wt% of at least one saturated mono- or dicarboxylic acid with 6 to 50 carbon atoms,

A2) 1 to 99 wt% of at least one unsaturated mono- or dicarboxylic acid with 6 to 50 carbon atoms,

and

B) At least one polar nitrogen-containing compound that is active as a paraffin disperser in middle distillates in an amount from 0.1 to 90 wt% with respect to the total weight of A1, A2 and B.

Another object of the invention consists of low temperature stabilized solutions of the additives in accordance with the invention in organic solvents, where the solutions contain 1 to 90 wt% solvent. Suitable solvents are aliphatic and/or aromatic hydrocarbons or hydrocarbon mixtures. Preferably, the additives in accordance with the invention contain 1-80%, especially 10-70%, particularly 25-60% solvent. The low temperature stabilized solutions in accordance with the invention have a pour point under  $-40^{\circ}\text{C}$ , preferably  $-45^{\circ}\text{C}$ , especially  $-50^{\circ}\text{C}$ .

Another object of the invention consists of low temperature stabilized fatty acid mixtures of

A1) 1 to 99 wt% of at least one saturated mono- or dicarboxylic acid with 6 to 50 carbon atoms,

A2) 1 to 99 wt% of at least one unsaturated mono- or dicarboxylic acid with 6 to 50 carbon atoms,

and

B) At least one polar nitrogen-containing compound that is active as a paraffin disperser in middle distillates in an amount from 0.01 to 90 wt% with respect to the total weight of A1, A2 and B.

Another object of the invention consists of fuels that contain, besides a middle distillate with up to 0.05 wt% sulfur content, fatty acid mixtures of

A1) 1 to 99 wt% of at least one saturated mono- or dicarboxylic acid with 6 to 50 carbon atoms,

A2) 1 to 99 wt% of at least one unsaturated mono- or dicarboxylic acid with 6 to 50 carbon atoms,

and

B) At least one polar nitrogen-containing compound that is active as a paraffin disperser in middle distillates in an amount from 0.01 to 90 wt% with respect to the total weight of A1, A2 and B.

Another object of the invention is the use of the said mixture of said components A and B to improve the lubricant properties of low sulfur middle distillates that have a sulfur content up to 0.05 wt%.

Preferred fatty acids (component A) are ones with 8-40 C atoms, especially 12-22 C atoms. The alkyl residues of the fatty acids essentially consist of carbon and hydrogen. However, they can have other substituents such as hydroxy, halogen, amino or nitro groups, provided these do not adversely affect the predominant hydrocarbon character.

Component A2 can contain one or more double bond and can be of natural or synthetic origin. In the case of polyunsaturated carboxylic acid, their double bonds can be isolated or even conjugated. The amount of saturated acids A1 in the mixture of A1 and A2 is preferably under 20 wt%, especially under 10 wt%, preferably under 5 wt%. In preferred fatty acid mixtures, which is understood here to mean the combination of A1 and A2, at least 50 wt%, especially at least 75 wt%, particularly at least 90 wt% of the components contain one or more double bonds. These preferred fatty acid (mixtures) have iodine number of at least 40 g I/100 g, preferably at least 80 g I/100 g, especially at least 125 g I/100 g.

Suitable fatty acids are, for example, lauric, tridecanoic, myristic, pentadecanoic, palmitic, margaric, stearic, isostearic, arachic and behenic acids, oleic and erucic acid, palmitoleic, myristoleic, linoleic, linolenic, elaeosteric and arachidonic acid, ricinoleic acid as well as fatty acid mixtures obtained from natural fats and oils such as coconut oil, peanut oil, fish oil, linseed oil, palm oil, rapeseed oil, dehydrated castor oil, castor oil, colza oil, soy oil, sunflower seed oil and tall oil fatty acid.

Also suitable are dicarboxylic acids like dimer fatty acids and alkyl and alkenylsuccinic acids with C<sub>8</sub>-C<sub>50</sub> alk(en)yl residues, preferably with C<sub>8</sub>-C<sub>40</sub>, especially C<sub>12</sub>-C<sub>22</sub> alkyl residues. The alkyl residues can be linear as well as branched (oligomerized alkenes, PIB).

The fatty acids can additionally contain 1-40, particularly 1-25 wt% resin acids, with respect to the weight of A1 and A2 together.

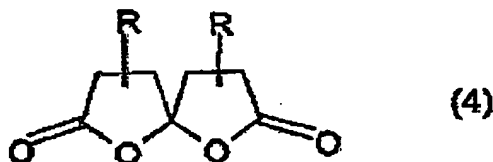
The additives in accordance with the invention contain as component B at least one polar nitrogen-containing compound that is effective as a paraffin disperser in middle distillates.

Paraffin dispersers reduce the size of the paraffin crystals that form at low temperatures and keep the paraffin particles from settling out, but rather cause them to remain colloiddally dispersed with a clearly reduced tendency to settle. Oil-soluble polar compounds with ionic or polar groups, for example amine salts and/or amides, which are obtained by the reaction of aliphatic or aromatic amines, preferably long-chain aliphatic amines, with aliphatic or aromatic mono-, di-, tri- or tetracarboxylic acids or their anhydrides, have proved to be good paraffin dispersers. Especially preferred paraffin dispersers contain reaction products of secondary fatty amines with 8 to 36 C atoms, especially dicoco fatty amine, ditallow fatty amine and distearylamine. Other paraffin dispersers are copolymers of maleic anhydride and  $\alpha,\beta$ -unsaturated compounds, which likewise can be reacted with primary monoalkylamines and/or aliphatic alcohols, the reaction products of alkenylspirobis lactones with amines and the reaction products of terpolymers based on  $\alpha,\beta$ -unsaturated dicarboxylic anhydrides,  $\alpha,\beta$ -unsaturated compounds and polyoxyalkylene ethers of lower unsaturated alcohols. Alkylphenol-formaldehyde resins are also suitable as paraffin dispersers. Some suitable paraffin dispersers are listed below.

The paraffin dispersers mentioned below are in part prepared by the reaction of compounds that contain an acyl group, with an amine. This amine is a compound of the formula  $NR^6R^7R^8$ , in which  $R^6$ ,  $R^7$  and  $R^8$  can be the same or different, and at least one of these groups stands for  $C_8$ - $C_{36}$  alkyl,  $C_8$ - $C_{36}$  cycloalkyl,  $C_8$ - $C_{36}$  alkenyl, especially  $C_{12}$ - $C_{24}$  alkyl,  $C_{12}$ - $C_{24}$  alkenyl or cyclohexyl, and the other groups either mean hydrogen,  $C_1$ - $C_{36}$  alkyl,  $C_2$ - $C_{36}$  alkenyl, cyclohexyl, or a group of the formula  $-(A-O)_x-E$  or  $-(CH_2)_n-NYZ$ , in which A stands for an ethylene or propylene group,  $x$  is a number from 1 to 50,  $E = H$ ,  $C_1$ - $C_{30}$  alkyl,  $C_5$ - $C_{12}$  cycloalkyl or  $C_6$ - $C_{30}$  aryl, and  $n$  means 2, 3 or 4, and Y and Z independently mean H,  $C_1$ - $C_{30}$  alkyl or  $-(A-O)_x$ . Acyl group here is understood to mean a functional group of the following formula:

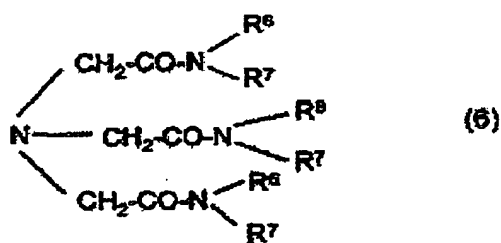
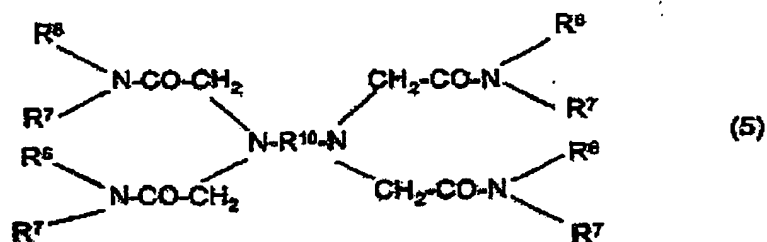


1. Reaction products of alkenylspirobis lactones of formula 4



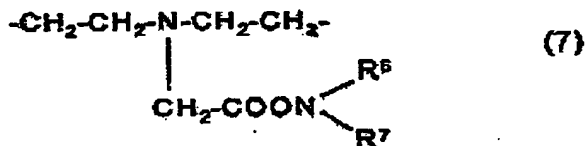
where each R represents  $C_8$ - $C_{200}$  alkenyl, with amines of the formula  $NR^6R^7R^8$ . Suitable reaction products are listed in EP-A-0 413 279. According to reaction conditions one obtains amides or amide ammonium salts in the reaction of compounds of formula (4) with the amines.

2. Amides or ammonium salts of aminoalkylenepolycarboxylic acid with secondary amines of formulas 5 and 6

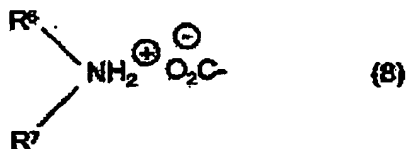


in which

$\text{R}^{10}$  means a linear or branched alkenyl residues with 2 to 6 carbon atoms or a residue of formula 7



in which  $\text{R}^6$  and  $\text{R}^7$  mean in particular alkyl residues with 10 to 30, preferably 14 to 24 C atoms, where the amide structure can also partially or completely be in the form of the ammonium salt structure of formula 8

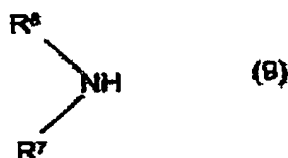


The amides or amide ammonium salts or ammonium salts of, for example, nitrilotriacetic acid, ethylenediaminetetraacetic acid or propylene-1,2-diaminetetraacetic acid are obtained by the reaction of the acids with 0.5 to 1.5 mol amine, preferably 0.8 to 1.2 mol amine, per carboxyl



group. The reaction temperatures are about 80 to 200°C, and in the preparation of the amides continuous removal of the resulting reaction water takes place. The reaction, however, need not be entirely directed toward the amide, rather 0 to 100 mol% of the amine that is used can be in the form of the ammonium salt. The compounds mentioned under B1 can also be prepared under analogous conditions.

Possibilities as amines of formula 9



are in particular dialkylamines in which  $\text{R}^6$  and  $\text{R}^7$  mean a linear alkyl residue with 10 to 30 carbon atoms, preferably 14 to 24 carbon atoms. In particular one may mention dioleylamine, dipalmitylamine, dicoco fatty amine and dibehenylamine and preferably ditallow fatty amine.

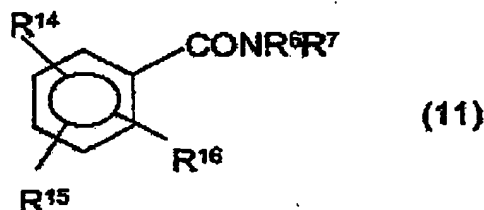
Quaternary ammonium salts of formula 10



where  $\text{R}^6$ ,  $\text{R}^7$  and  $\text{R}^8$  have the meaning given above and  $\text{R}^{11}$  stands for  $\text{C}_1$ - $\text{C}_{30}$ , preferably  $\text{C}_1$ - $\text{C}_{22}$  alkyl,  $\text{C}_1$ - $\text{C}_{30}$  alkenyl, preferably  $\text{C}_1$ - $\text{C}_{22}$  alkenyl, benzyl or a residue of the formula  $-(\text{CH}_2-\text{CH}_2\text{O})_n-\text{R}^{12}$ , where  $\text{R}^{12}$  is hydrogen or a fatty acid residue of the formula  $\text{C}(\text{O})-\text{R}^{13}$ , where  $\text{R}^{13}$  is  $\text{C}_6$ - $\text{C}_{40}$  alkenyl,  $n$  is a number from 1 to 30 and  $\text{X}$  stands for halogen, preferably chlorine, or a methosulfate.

One may mention as examples of such quaternary ammonium salts: dihexadecyl dimethylammonium chloride, distearyl dimethylammonium chloride, quaternization products of esters of di- and triethanolamine with long-chain fatty acids (lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, oleic acid and fatty acid mixtures such as coco fatty acid, tallow fatty acid, hydrogenated tallow fatty acid, tall oil fatty acid) such as N-methyltriethanolammonium distearyl ester chloride, N-methyltriethanolammonium distearyl ester methosulfate, N,N-dimethyldiethanolammonium distearyl ester chloride, N-methyltriethanolammonium dioleyl ester chloride, N-methyltriethanolammonium trilauryl ester methosulfate, N-methyltriethanolammoniumtristearyl ester methosulfate and their mixtures.

#### 4. Compounds of formula 11



in which  $R^{14}$  stands for  $CONR^6R^7$  or  $CO_2^-H_2NR^6R^7$ ,  $R^{15}$  and  $R^{16}$  stand for H,  $CONR^{17}_2$ ,  $CO_2R^{17}$  or  $OCOR^{17}$ ,  $-OR^{17}$ ,  $-R^{17}$  or  $NCOR^{17}$ , and  $R^{17}$  is alkyl, alkoxyalkyl or polyalkoxyalkyl and has at least 10 carbon atoms.

Preferred carboxylic acids or acid derivatives are phthalic acid (anhydride), trimellitol, pyromellitol (dianhydride), isophthalic acid, terephthalic acid, cyclohexane dicarboxylic acid (anhydride), maleic acid (anhydride), alkenylsuccinic acid (anhydride). The "anhydride" in parenthesis means that the anhydrides of the said acids are also preferred acid derivatives.

If the compounds of formula (11) are amides or amine salts, they are preferably those of a secondary amine that contains a group that contains hydrogen and carbon and has at least 10 carbon atoms.

It is preferable for  $R^{17}$  to contain 10 to 30, especially 10 to 22, for example 14 to 20, carbon atoms and preferably to be linear or branched in position 1 or 2. The other groups that contain hydrogen and carbon can be shorter, for example they can contain fewer than 6 carbon atoms, or, if desired, they can have at least 10 carbon atoms. Suitable alkyl groups include methyl, ethyl, propyl, hexyl, decyl, dodecyl, tetradecyl, eicosyl and docosyl (behenyl).

In addition, polymers that contain at least one amide or ammonium group directly bonded to the polymer backbone are suitable, where the amide or ammonium group carries at least one alkyl group with at least 8 C atoms at a nitrogen atom. Such polymers can be produced in various ways. One way is to use a polymer that contains a number of carboxylic acid or anhydride groups and reacting this polymer with an amine of the formula  $NHR^6R^7$  in order to obtain the desired polymer.

In addition, copolymers of unsaturated esters like  $C_1$ - $C_{40}$  alkyl (meth)acrylates, fumaric acid dye ( $C_1$ - $C_{40}$  alkyl esters),  $C_1$ - $C_{40}$  alkyl vinyl ethers,  $C_1$ - $C_{40}$  alkyl vinyl esters or  $C_2$ - $C_{40}$  olefins (linear, branched, aromatic) with unsaturated carboxylic acids or their reactive derivatives, such as carboxylic anhydrides (acryl acid, methacrylic acid, maleic acid, fumaric acid, tetrahydrophthalic acid, citraconic acid, preferably maleic anhydride) are generally suitable as polymers.

Carboxylic acids are preferably reacted with 0.1 to 1.5 mol, especially 0.5 to 1.2 mol amine, per acid group, carboxylic anhydrides are preferably reacted with 0.1 to 2.5, especially

0.5 to 2.2, mol of amine per acid anhydride group, with amides, ammonium salts, amide-ammonium salts or imides resulting in each case according to the reaction conditions. Thus copolymers that contain unsaturated carboxylic anhydrides yield half amide and half amine salts in a reaction with a secondary amine due to the reaction with the anhydride group. Water can be eliminated by heating, with the formation of the diamide.

Especially suitable examples of an amide group containing polymers for use in accordance with the invention are:

5. Copolymers (a) of a dialkyl fumarate, maleate, citraconate or itaconate with maleic anhydride, or (b) copolymers of vinyl esters, for example vinyl acetate or vinyl stearate, with maleic anhydride, or (c) copolymers of a dialkyl fumarate, maleate, citraconate or itaconate with maleic anhydride and vinyl acetate.

Especially suitable examples of these polymers are copolymers of didodecyl fumarate, vinyl acetate and maleic anhydride; ditetradecyl fumarate, vinyl acetate and maleic anhydride; dihexadecyl fumarate, vinyl acetate and maleic anhydride; or the corresponding copolymers in which the itaconate is used instead of the fumarate.

In the above examples of suitable polymers, the desired amide is obtained by the reaction of the polymer that contains anhydride groups with a secondary amine of the formula  $\text{HNR}^6\text{R}^7$  (optionally additionally with an alcohol, if an ester amide has been formed). If polymers that contain one anhydride are reacted the resulting amino groups will be ammonium salts and amides. Such polymers can be used with the stipulation that they contain at least two amide groups.

It is important that the polymer, which contains at least two amide groups, contain at least one alkyl group with at least 10 carbon atoms. This long-chain group, which can be a linear or branched alkyl group, can be bonded via the nitrogen atom of the amide group.

The amines that are suitable for this can be represented by the formula  $\text{R}^6\text{R}^7\text{NH}$  and the polyamines can be represented by  $\text{R}^6\text{NH}[\text{R}^{19}\text{NE}]_x\text{R}^7$ , where  $\text{R}^{19}$  is a divalent hydrocarbon group, preferably an alkylene or hydrocarbon-substituted alkylene group, and  $x$  is a whole number, preferably between 1 and 30. Preferably one of the two or both residues  $\text{R}^6$  and  $\text{R}^7$  contains at least 10 carbon atoms, preferably 10 to 20 carbon atoms, for example dodecyl, tetradecyl, hexadecyl, or octadecyl.

Examples of suitable secondary amines are dioctylamine and ones that contain alkyl groups with at least 10 carbon atoms, for example didecylamine, didodecylamine, dicoco amine (i.e., mixed  $\text{C}_{12}$ - $\text{C}_{14}$  amine), dioctadecylamine, hexadecyloctadecylamine, di-(hydrogenated tallow)-amine (roughly 4 wt%  $n$ - $\text{C}_{14}$ -alkyl, 30 wt%  $n$ - $\text{C}_{10}$ -alkyl, 60 wt%  $n$ - $\text{C}_{18}$ -alkyl, with the remainder being unsaturated).

Examples of suitable polyamines are N-octadecylpropanediamine, N,N'-dioctadecylpropanediamine, N-tetradecylbutanediamine and N,N'-dihexadecylhexanediamine, N-cocopropylenediamine (C<sub>12</sub>/C<sub>14</sub>-alkylpropylenediamine), N-tallow propylenediamine (C<sub>16</sub>/C<sub>18</sub>-alkylpropylenediamine).

The amide-containing polymers usually have an average molecular weight (number average) from 1000 to 500,000, for example 10,000 to 100,000.

6. Copolymers of styrene, its derivatives or aliphatic olefins with 2 to 40 C atoms, preferably with 6 to 20 C atoms, and olefinically unsaturated carboxylic acids or carboxylic anhydrides that are reacted with amines of the formula HNR<sup>6</sup>R<sup>7</sup>. The reaction can be carried out before or after the polymerization.

In detail, the structural units of the copolymers derive from, for example, maleic acid, fumaric acid, tetrahydrophthalic acid, citraconic acid, preferably maleic anhydride. They can be used both in the form of their homopolymers and in the form of the copolymers. Following are suitable as comonomers: styrene and alkylstyrenes, linear and branched olefins with 2 to 40 carbon atoms, and their mixtures with each other. One may mention as examples: styrene,  $\alpha$ -methylstyrene, dimethylstyrene,  $\alpha$ -ethylstyrene, diethylstyrene, isopropylstyrene, tert-butylstyrene, ethylene, propylene, n-butylene, diisobutylene, decene, dodecene, tetradecene, hexadecene, octadecene. Styrene and isobutene are preferred, with styrene being especially preferred.

In particular, one may mention as examples of polymers: polymaleic acid, a molar, alternately structured styrene/maleic acid copolymer, statistically structured styrene/maleic acid copolymers in a 90:10 ratio and an alternating copolymer of maleic acid and isobutene. The molecular weights of the polymers are in general 500 g/mol to 20,000 g/mol, preferably 700 to 2000 g/mol.

The reaction of the polymers or copolymers with the amines takes place at temperatures from 50 to 200°C over 0.3 to 30 hours. The amine in this case is used in amounts of roughly 1 mol per mol of dicarboxylic anhydride that is incorporated by polymerization, i.e., about 0.9 to 1.1 mol/mol. Larger or smaller amounts can be used, but do not bring any advantage. If amounts larger than one mol are used, one obtains in some cases ammonium salts, since the formation of a second amide group requires higher temperatures, longer residence times and removal of water. If amounts smaller than one mol are used, complete conversion to the monoamide does not take place and one obtains a correspondingly reduced activity.

Instead of the subsequent reaction of the carboxyl groups in the form of the dicarboxylic anhydride with amines to form the corresponding amides it can sometimes be advantageous to produce the monoamides of the monomers and then to incorporate them by polymerization directly during the polymerization. Mostly, however, this is industrially much more costly, since

the amines can add to the double bond of the monomer mono- and dicarboxylic acid and then copolymerization is no longer possible.

7. Copolymers consisting of 10 to 95 mol% of one or more alkyl acrylates or alkyl methacrylates with  $C_1$ - $C_{26}$  alkyl chains and of 5 to 90 mol% of one or more ethylenically unsaturated dicarboxylic acids or their anhydrides, where the copolymer is largely reacted with one or more primary or secondary amines to form a monoamide or amide/ammonium salt of the dicarboxylic acid.

The copolymers consist of 10 to 95 mol%, preferably 40 to 95 mol% and especially preferably 60 to 90 mol%, of alkyl (meth)acrylates and 5 to 90 mol%, preferably 5 to 60 mol% and especially preferably 10 to 40 mol% of the olefinically unsaturated dicarboxylic acid derivatives. The alkyl groups of the alkyl (meth)acrylates contain from 1 to 26, preferably 4 to 22 and especially preferably 8 to 18 carbon atoms. They are preferably linear unbranched. However, they can contain up to 20 wt% cyclic and/or branched fractions.

Examples of especially preferred alkyl (meth)acrylates are n-octyl (meth)acrylate, n-decyl (meth)acrylate, n-dodecyl (meth)acrylate, n-tetradecyl (meth)acrylate, n-hexadecyl (meth)acrylate and n-octadecyl (meth)acrylate, and the mixtures thereof.

Examples of ethylenically unsaturated dicarboxylic acids are maleic acid, tetrahydrophthalic acid, citraconic acid and itaconic acid or their anhydrides and fumaric acid. Maleic anhydride is preferred.

Compounds of the formula  $HNR^6R^7$  are possibilities as amines.

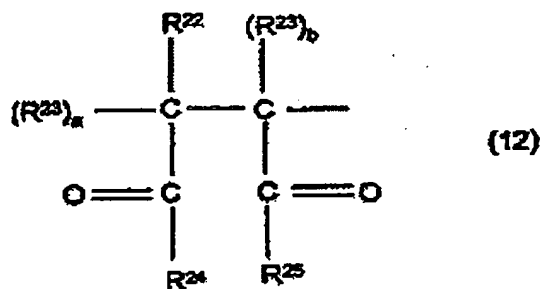
As a rule, it is advantageous in the copolymerization to use the dicarboxylic acids in the form of the anhydrides, if available, for example maleic anhydride, itaconic anhydride, citraconic anhydride and tetrahydrophthalic anhydride, since the anhydrides as a rule copolymerize better with the (meth)acrylates. The anhydride groups of the copolymers can then be reacted directly with the amines. The reaction of the polymers with the amines takes place at temperatures from 50 to 200°C over 0.3 to 30 hours. The amine is used in amounts of roughly one to two mol per mol of dicarboxylic acid that is incorporated by polymerization, i.e., about 0.9 to 2.1 mol/mol. The use of greater or lesser amounts is possible, but does not bring any advantage. If amounts larger than 2 mol are used, free amine will be present. If amounts smaller than one mol are used, complete reaction to monoamide does not take place and one obtains correspondingly reduced activity.

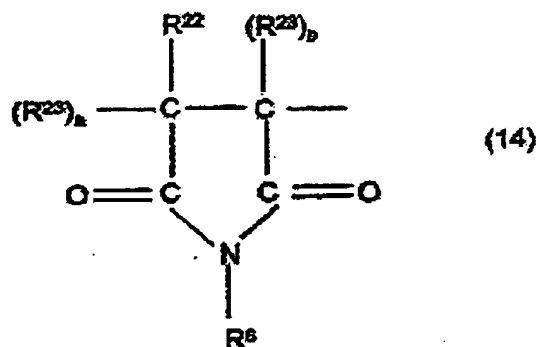
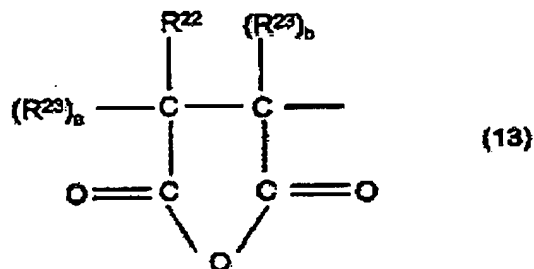
In some cases it can be advantageous if the amide/ammonium salt structure is formed from two different amines. For example, a copolymer of lauryl acrylate and maleic anhydride can first be reacted with a secondary amine like hydrogenated ditallow fatty amine to form an amide, after which the free carboxyl group that comes from the anhydride can be neutralized with another amine, for example 2-ethylhexylamine, to form an ammonium salt. The reverse

procedure is just as possible: first the reaction is carried out with ethylhexylamine to form the monoamide, and then the reaction is carried out with ditallow fatty amine to form the ammonium salt. Preferably at least one amine that has at least one linear, unbranched alkyl group of more than 16 carbon atoms is used. It is not important if this amine is present in the synthesis of the amide structure or is present as ammonium salt of the dicarboxylic acid.

Instead of the subsequent reaction of the carboxyl groups or the dicarboxylic anhydride with amines to form the corresponding amides or amide/ammonium salts, in some cases it can be advantageous to produce the monoamides or amide/ammonium salts of the monomers and then to incorporate them directly by polymerization in the polymerization. However, in most cases it is industrially more costly, since the amines can add to the double bond of the monomer dicarboxylic acid and then copolymerization is not longer possible.

8. Terpolymers based on  $\alpha,\beta$ -unsaturated dicarboxylic anhydrides,  $\alpha,\beta$ -unsaturated compounds and polyoxyalkylene ethers of lower unsaturated alcohols, which are characterized by the fact that they contain 20-80, preferably 40-60 mol% bivalent structural units of the formulas 12 and/or 14 and optionally 13, where the structural units 13 derive from unreacted anhydride residues,





where

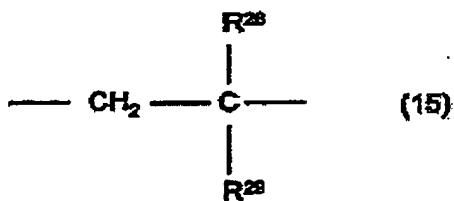
$R^{22}$  and  $R^{23}$  independently mean hydrogen or methyl,

$a$  and  $b$  are equal to nil or one or  $a + b$  is equal to one,

$R^{24}$  and  $R^{25}$  are the same or different and stand for the groups  $-NHR^6$ ,  $N(R^6)_2$  and/or  $-OR^{27}$ , and

$R^{27}$  stands for a cation of the formula  $H_2N(R^6)_2$  or  $H_3NR^6$ ,

19-80 mol%, preferably 39-60 mol% bivalent structural units of formula 15

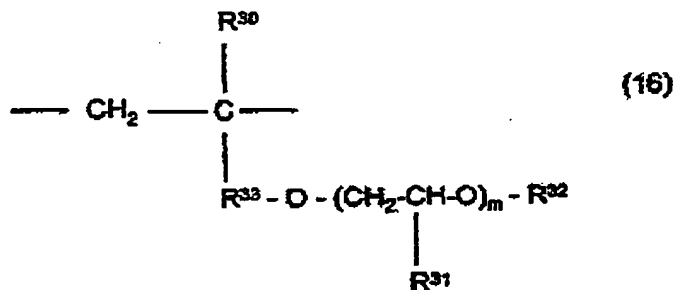


in which

$R^{28}$  means hydrogen or  $C_1$ - $C_4$  alkyl and

$R^{29}$  means  $C_6$ - $C_{60}$  alkyl or  $C_6$ - $C_{18}$  aryl and

1-30 mol%, preferably 1-20 mol%, bivalent structural units of formula 16



in which

R<sup>30</sup> means hydrogen or methyl,

R<sup>31</sup> means hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl,

R<sup>33</sup> means C<sub>1</sub>-C<sub>4</sub> alkylene,

m is a number from 1 to 100,

R<sup>32</sup> means C<sub>1</sub>-C<sub>24</sub> alkyl, C<sub>5</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>18</sub> aryl or -C(O)-R<sup>34</sup>, where

R<sup>34</sup> mean C<sub>1</sub>-C<sub>40</sub> alkyl, C<sub>5</sub>-C<sub>10</sub> cycloalkyl or C<sub>6</sub>-C<sub>18</sub> aryl.

The said alkyl, cycloalkyl and aryl residues can optionally be substituted. Suitable substituents on the alkyl and aryl residues are, for example, (C<sub>1</sub>-C<sub>6</sub>)-alkyl, halogens like fluorine, chlorine, bromine and iodine, preferably chlorine, and (C<sub>1</sub>-C<sub>6</sub>)-alkoxy.

Alkyl in this case stands for a linear or branched hydrocarbon residue. In particular the following may be mentioned: n-butyl, tert-butyl, n-hexyl, n-octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, dodecenyl, tetrapropenyl, tetradecenyl, pentapropenyl, hexadecenyl, octadecenyl and eicosanyl, or mixtures like coco alkyl, tallow fatty alkyl and behenyl.

Cycloalkyl here stands for a cyclic aliphatic residue with 5 to 20 carbon atoms. Preferred cycloalkyl residues are cyclopentyl and cyclohexyl.

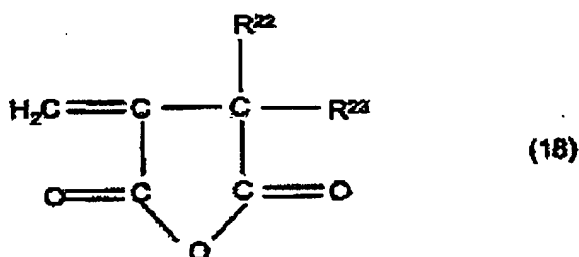
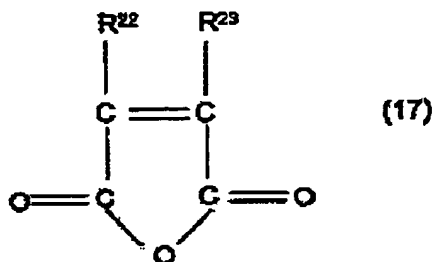
Aryl here stands for an optionally substituted aromatic ring system with 6 to 18 carbon atoms.

The terpolymers consist of the bivalent structural units of formulas 12 and 14 and 15 and 16 and optionally 13. They contain only the end groups that result from initiation, inhibition and chain termination in polymerization in a substantially known way.

In particular, structural units of formulas 12 to 14 derive from α,β-unsaturated dicarboxylic anhydrides of the formulas 17 and 18

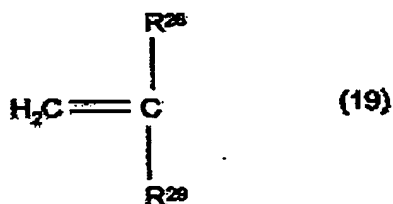


15



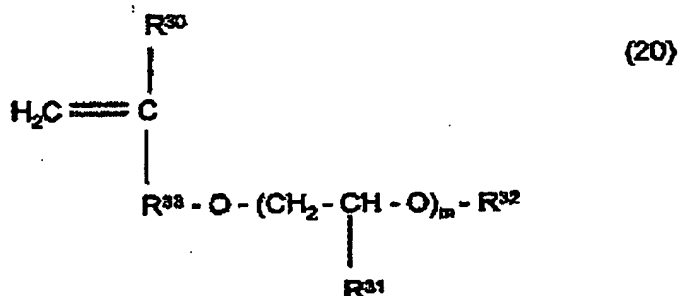
such as maleic anhydride, itaconic anhydride, citraconic anhydride, preferably maleic anhydride.

The structural units of formula 15 derive from the  $\alpha,\beta$ -unsaturated compounds of formula 19.



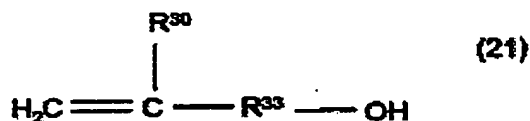
One may mention as examples the following  $\alpha,\beta$ -unsaturated olefins: styrene,  $\alpha$ -methylstyrene, dimethylstyrene,  $\alpha$ -ethylstyrene, diethylstyrene, isopropylstyrene, tert-butylstyrene, diisobutylene and  $\alpha$ -olefins, like decene, dodecene, tetradecene, pentadecene, hexadecene, octadecene,  $C_{20}$ - $\alpha$ -olefin,  $C_{24}$ - $\alpha$ -olefin,  $C_{30}$ - $\alpha$ -olefin, tripropenyl, tetrapropenyl, pentapropenyl, and their mixtures.  $\alpha$ -Olefins with 10 to 24 C atoms and styrene are preferred, and  $\alpha$ -olefins with 12 to 20 atoms are especially preferred.

The structural units of formula 16 derive from polyoxyalkylene ethers of lower unsaturated alcohols of formula 20



The monomers of formula 20 are etherification products ( $\text{R}^{32} = -\text{C}(\text{O})\text{R}^{34}$ ) or esterification products ( $\text{R}^{32} = -\text{C}(\text{O})\text{R}^{34}$ ) of polyoxyalkylene ethers ( $\text{R}^{32} = \text{H}$ ).

The polyoxyalkylene ethers ( $\text{R}^{32} = \text{H}$ ) can be prepared by known methods by addition of  $\alpha$ -olefin oxides like ethylene oxide, propylene oxide and/or butylene oxide to polymerizable lower, unsaturated alcohols of formula 21

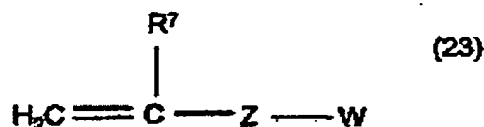


Such polymerizable lower unsaturated alcohols are, for example, allyl alcohol, methallyl alcohol, butenols, like 3-buten-1-ol and 1-buten-3-ol or methylbutenols like 2-methyl-3-buten-1-ol, 2-methyl-3-buten-2-ol and 3-methyl-3-buten-1-ol. Addition products of ethylene oxide and/or propylene oxide to allyl alcohol are preferred.

A subsequent etherification of these polyoxyalkylene ethers to compounds of formula 20 with  $\text{R}^{32} = \text{C}_1\text{-C}_{24}$  alkyl, cycloalkyl or aryl takes place by substantially known methods. Suitable methods are known, for example, from J. March, *Advanced Organic Chemistry*, 2<sup>nd</sup> Edition, p. 357 ff (1977). These etherification products of the polyoxyalkylene ethers can also be prepared by adding  $\alpha$ -olefin oxides, preferably ethylene oxide, propylene oxide and/or butylene oxide, to alcohols of formula 22



in which  $\text{R}^{32}$  is  $\text{C}_1\text{-C}_{24}$  alkyl,  $\text{C}_5\text{-C}_{20}$  cycloalkyl or  $\text{C}_6\text{-C}_{18}$  aryl, by known methods and reacting them with the polymerizable lower unsaturated halides of formula 23



where W stands for a halogen atom. The chlorides and bromides are preferably used as halides. Suitable preparation methods are indicated, for example, in J. March, *ibid*. The esterification of polyoxyalkylene ethers ( $\text{R}^{32} = -\text{C}(\text{O})-\text{R}^{34}$ ) takes place by reaction with common esterification agents like carboxylic acids, carboxylic halides, carboxylic anhydrides or carboxylates with  $\text{C}_1$ - $\text{C}_4$  alcohols. Preferably, the halides and anhydrides of  $\text{C}_1$ - $\text{C}_{40}$  alkyl,  $\text{C}_5$ - $\text{C}_{10}$  cycloalkyl or  $\text{C}_6$ - $\text{C}_{18}$ -arylcarboxylic acids are used. The esterification is generally carried out at temperatures from 0 to 200°C, preferably 10 to 100°C.

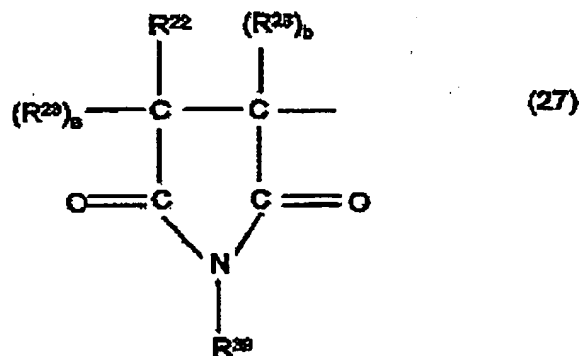
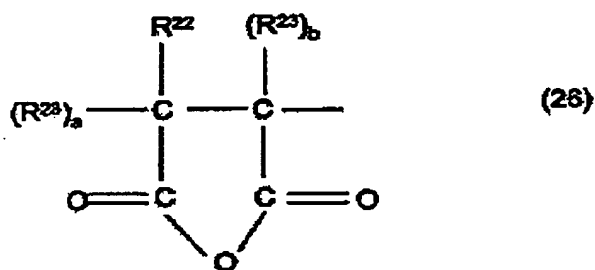
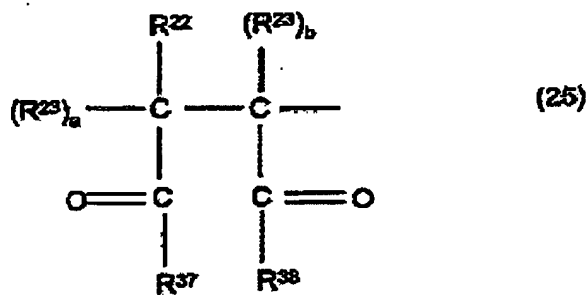
In the monomers of formula 20, the subscript m means the degree of alkoxylation, i.e., the number of mols of  $\alpha$ -olefin that are added per mol of formula 20 or 21.

The following may be mentioned as examples of primary amines that are suitable for preparation of the terpolymers: n-hexylamine, n-octylamine, n-tetradecylamine, n-hexadecylamine, n-stearylamine or also N,N-dimethylaminopropylenediamine, cyclohexylamine, dehydroabietylamine and their mixtures.

The following may be mentioned as examples of secondary amines that are suitable for preparation of the terpolymers: didecylamine, ditetradecylamine, distearylamine, dicocos fatty amine, ditallow fatty amine, and their mixtures.

The terpolymers have K values (measured in accordance with Übbelohde in a 5 wt% solution in toluene at 25°C) of 8 to 100, preferably 8 to 50, which correspond to average molecular weights ( $M_w$ ) between about 500 and 100,000. Suitable examples are listed in EP 606 055.

9. Reaction products of alkanolamines and/or polyether amines with polymers that contain dicarboxylic anhydride groups, which are characterized by the fact that they contain 20-80, preferably 40-60 mol% bivalent structural units of formulas 25 and 27 and optionally 26.



where

$\text{R}^{22}$  and  $\text{R}^{23}$  independently mean hydrogen or methyl,

$a, b$  are equal to nil or 1 and  $a + b$  is equal to 1,

$\text{R}^{37} = -\text{OH}, -\text{O}-[\text{C}_1-\text{C}_{30}\text{-alkyl}], \text{NR}^6\text{R}^7, -\text{O}^5\text{N}^5\text{R}^6\text{R}^7\text{H}_2$

$\text{R}^{38} = \text{R}^{37}$  or  $\text{NR}^6\text{R}^{39}$

$\text{R}^{39} = -(\text{A}-\text{O})_x-\text{E}$

with

$\text{A} = \text{ethylene or propylene group}$

$x = 1$  to 50

$E = H, C_1-C_{30}$ -alkyl,  $C_5-C_{12}$ -cycloalkyl or  $C_6-C_{30}$ -aryl

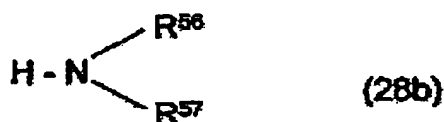
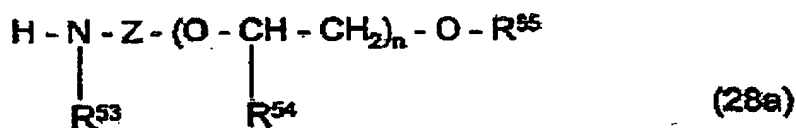
and

80-20, preferably 60-40 mol% bivalent structural units of formula 15.

In particular, the structural units of formulas 25, 26, and 27 derive from  $\alpha$ - $\beta$ -unsaturated dicarboxylic anhydrides of formulas 17 and/or 18.

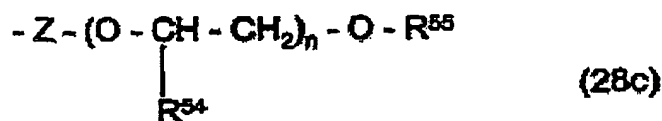
The structural units of formula 15 derive from the  $\alpha$ , $\beta$ -unsaturated olefins of formula 19. The said alkyl, cycloalkyl and aryl residues have the same meanings as under 8.

Residues  $R^{37}$  and  $R^{38}$  in formula 25 or  $R^{39}$  in formula 27 derive from polyether amines or alkanolamines of formulas 28 a) and b), amines of the formula  $NR^6R^7R^8$  and optionally from alcohols with 1 to 30 carbon atoms.



Here

$R^{55}$  means hydrogen,  $C_6-C_{40}$ -alkyl or



$R^{54}$  means hydrogen,  $C_1-C_4$ -alkyl

$R^{55}$  means hydrogen,  $C_1$  to  $C_4$  alkyl,  $C_5$  to  $C_{12}$  cycloalkyl or  $C_6$  to  $C_{30}$  aryl,

$R^{56}$ ,  $R^{57}$  independently mean hydrogen,  $C_1$  to  $C_{22}$  alkyl,  $C_2$  to  $C_{22}$  alkenyl or  $Z-OH$

$Z$  means  $C_2$  to  $C_4$  alkylene, and

$n$  is a number between 1 and 1000.

For derivatization of the structural units of formulas 17 and 18, preferably in mixtures of at least 50 wt% alkylamines of the formula  $HNR^6R^7R^8$  and at most 50 wt% polyether amines, alkanolamines of formulas 28 a) and b) were used.

Preparation of the polyether amines is possible, for example, by reductive amination of polyglycols. In addition, the preparation of polyether amines with a primary amino group can be done by addition of polyglycols to acrylonitrile followed by catalytic hydrogenation. Moreover, polyether amines are accessible by the reaction of polyethers with phosgene thionyl chloride and subsequent amination of polyether amine. The polyether amines used in accordance with the invention are commercially available, for example, under the name Jeffamine® (Texaco). The molecular weight is up to 2000 g/mol and the ethylene oxide/propylene oxide ratio is from 1:10 to 6:1. Another possibility for derivatization of the structural units of formulas 17 and 18 is to use an alkanolamine of formula instead of the polyether amines and then carrying out an oxalkylation.

0.01 to 2 mol, preferably 0.01 to 1 mol alkanolamine is used per mol of anhydride. The reaction mixture is between 50 and 100°C (amide formation). In the case of primary amines the reaction takes place at temperatures above 100°C (imide formation).

The oxalkylation usually takes place at temperatures between 70 and 170°C with catalysis by bases like NaOH or NaOCH<sub>3</sub>, supplying gaseous alkylene oxides like ethylene oxides (EO) and/or propylene oxide (PO). Usually 1 to 500, preferably 1 to 100 mol alkylene oxide is supplied per mol of hydroxyl groups.

One may mention as examples of suitable alkanolamines: monoethanolamine, diethanolamine, N-methylethanolamine, 3-aminopropanol, isopropanol, diglycolamine, 2-amino-2-methylpropanol and their mixtures.

One may mention as examples of primary amines: n-hexylamine, n-octylamine, n-tetradecylamine, n-hexadecylamine, n-stearylamine or also N,N-dimethylaminopropylenediamine, cyclohexylamine, dehydroabietylamine and their mixtures.

One may mention as examples of secondary amines: didecylamine, ditetradecylamine, distearylamine, dicoco fatty amine, ditallow fatty amine and their mixtures.

One may mention as examples of alcohols: methanol, ethanol, propanol, isopropanol, n-, sec-, tert-butanol, octanol, tetradecanol, hexadecanol, octadecanol, tallow fatty alcohol, behenyl alcohol, and their mixtures. Suitable examples are listed in EP-A-688 796.

10. Co- and terpolymers of N-C<sub>6</sub>-C<sub>24</sub>-alkylmaleiminide with C<sub>1</sub>-C<sub>30</sub>-vinyl esters, vinyl ethers and/or olefins with 1 to 30 C atoms, for example styrene or  $\alpha$ -olefins. These can be obtained, for one, by the reaction of a polymer containing an anhydride group with amines of the formula H<sub>2</sub>NR<sup>6</sup>, or by imidation of the dicarboxylic acid and subsequent copolymerization. The preferred dicarboxylic acid is maleic acid or maleic anhydride. Copolymers of 10 to 90 wt% C<sub>6</sub>-C<sub>24</sub>  $\alpha$ -olefins and 90 to 10 wt% N-C<sub>6</sub>-C<sub>22</sub>-alkylmaleicimide are preferred.

The mixture ratio between A and B can vary in wide limits. Even small amounts of B from 100 ppm to 50,000 ppm, preferably 1,000 ppm to 10,000 ppm are effective in fatty acid solutions as low temperature additive for A. They are capable of suppressing the inherent crystallization of the fatty acid, which leads to a lowering of the cloud point, or to prevent the sedimentation of crystals that have formed and in this way they enable problem-free management at reduced temperatures. For particular problem solutions, however, it is also possible for from 5% to 50%, in special cases up to 90%, of component B, with respect to the amount of component A, to be present. In this case in particular, the pour point and the lubricating capacity are improved. Accordingly, the preferred ratio of A to B is between 1:10 and 1:0.0001, especially between 1:4 and 1:0.0005, particularly between 1:1 and 1:0.001.

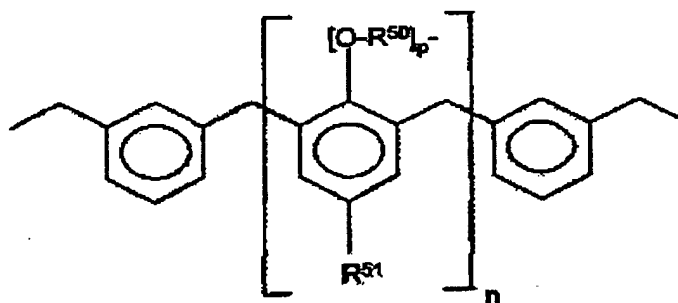
The additives in accordance with the invention are added to oils in amounts from 0.001 to 0.5 wt%, preferably 0.001 to 0.1 wt%. They can be used as such or can be dissolved in the solvents, for example aliphatic and/or aromatic hydrocarbons or hydrocarbon mixtures such as Toluene, xylene, ethylbenzene, decane, pentadecane, gasoline fractions, kerosene or commercial solvent mixtures like solvent naphtha, Shellsol AB®, Solvesso 150®, Solvesso 200®, Exxsol®, Isopar® and Shellsol D®. Preferably, the additives in accordance with the invention contain 1-80%, particularly 10-70%, especially 25-60% solvent. The additives which can even be used without any trouble at low temperatures of -40°C and lower, for example, improve the lubricity of the oils to which they are added as well as their low temperature and corrosion protection properties.

To produce additive packets for special problem, solutions the additives in accordance with the invention can also be used together with one or more oil-soluble coadditives, which used alone improve the low temperature flow properties and/or lubricating effect of crude oils, lubricating oils or fuel oils. Examples of such coadditives are copolymers containing vinyl acetate or terpolymers of ethylene, comb polymers, alkylphenol-aldehyde resins and oil-soluble amphiphils.

Thus, mixtures of the additives in accordance with the invention with copolymers that contain 10 to 40 wt% vinyl acetate and 60 to 90 wt% ethylene have shown excellent performance. According to another embodiment of the invention the additives in accordance with the invention are used in a mixture with ethylene/vinyl acetate/neononanoic acid vinyl ester terpolymers or ethylene/vinyl acetate/neodecanoic acid vinyl ester terpolymers to improve the flowability of mineral oils or mineral oil distillates. The terpolymers of the neononanoic acid vinyl esters or the neodecanoic acid vinyl esters contain 10 to 35 wt% vinyl acetate and 1 to 25 wt% of the relevant neo compound in addition to ethylene. Other preferred copolymers contain 0.5 to 20 wt% olefins such as diisobutylene, 4-methylpentene or norbornene in addition to ethylene and 10 to 35 wt% vinyl esters. The mixture ratio of the additives in accordance with

the invention with the said ethylene/vinyl acetate copolymers or the terpolymers of ethylene, vinyl acetate and the vinyl esters of neononanoic or neodecanoic acid amount to (in parts by weight) 20:1 to 1:20, preferably 10:1 to 1:10.

Thus, the additives in accordance with the invention can be together with alkylphenol-formaldehyde resins. In a preferred embodiment of the invention these alkylphenol-formaldehyde resins are ones of the formula



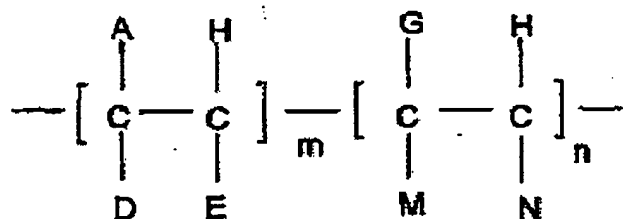
in which  $R^{50}$  stands for  $C_4$ - $C_{50}$  alkyl or alkenyl,  $R^{51}$  stands for ethoxy and/or propoxy,  $n$  stands for a number from 5 to 100 and  $p$  stands for a number from 0 to 50.

Finally, in another embodiment of the invention the additives in accordance with the invention can be used together with comb polymers. This is understood to mean polymers in which hydrocarbon residues with at least 8 and in particular at least 10 carbon atoms, are bonded to a polymer backbone. Preferably they are homopolymers whose alkyl side chains contain at least 8 and especially at least 10 carbon atoms. In the case of copolymers at least 20%, preferably at least 30% of the monomers have side chains (see: "Comb-like Polymers - Structure and Properties;" N. A. Platé and V. P. Shibaev, J. Polym. Sci. Macromolecular Revs. 1974, 8, 117 ff).

Examples of suitable comb polymers are, for example, fumarate/vinyl acetate copolymers (see EP 0 153 176 A1), copolymers of a  $C_6$ - $C_{24}$   $\alpha$ -olefin and a  $N$ - $C_6$ - $C_{22}$ -alkylmaleiminide (see EP 0 320 766), also esterified olefin/maleic anhydride copolymers, polymers and copolymers of  $\alpha$ -olefins and esterified copolymers of styrene and maleic anhydride.

Comb polymers can be described, for example, by the formula





Here,

A = R', COOR', OCOR', R"-COOR' or OR';

D = H, CH<sub>3</sub>, A or R;

E = H or A;

G = H, R', R"-COOR', an aryl or a heterocyclic residue;

M = H, COOR', OCOR', OR' or COOH;

N = H, R', COOR', OCOR', COOH or an aryl residue;

R' = a hydrocarbon chain with 8-150 carbon atoms;

R" = a hydrocarbon chain with 1 to 10 carbon atoms;

m = a number between 0.4 and 1.0; and

n = a number between 0 and 0.6.

The ratio of the mixture (in parts by weight) of the additives in accordance with the invention with resins or comb polymers is 1:10 to 20:1, preferably 1:1 to 10:1.

The additives in accordance with the invention are suitable for improving the lubricating properties of animal, vegetable, mineral or synthetic fuel oils at low dispensing rates. Moreover, they simultaneously improve the low-temperature and corrosion protective properties of oils to which they are added. The emulsification properties of the treated oils are less adversely affected than is the case with the lubricating additives of the prior art. The additives in accordance with the invention are especially well suited for use in middle distillates. Middle distillates are, in particular, those mineral oils that are obtained by distillation of crude oil and boil in the range from 120 to 450°C, for example kerosene, jet fuel, diesel and heating oil. These oils can also contain alcohols like methanol and/or ethanol or consist of them. Preferably, the additives in accordance with the invention are used in middle distillates that contain 0.05 wt% in less sulfur, especially preferably less than 350 ppm sulfur, in particular less than 200 ppm sulfur and in special cases less than 50 ppm sulfur. These are generally middle distillates that have been subjected to hydrofining and therefore contain only small amounts of the polyaromatic and polar compounds that give them a natural lubricating effect. The additives in accordance with the invention are additionally preferably used in middle distillates that have 95% distillation points

under 370°C, particularly 350°C and in special cases under 330°C. They can also be used as components in lubricating oils.

The mixtures can be used by themselves or also together with other additives, for example with other pour point lowering agents or dewaxing aids, with corrosion inhibitors, antioxidants, sludge inhibitors, dehazers, flow improvers, lubricity additives, and additives to reduce the cloud point. In addition, they are successfully used together with additive packets, which contain, among other things, known ash-free dispersion additives, detergents, defoamers, and corrosion inhibitors.

The improved low temperature stability and the effectiveness of the additives in accordance with the invention as lubricity additives are illustrated in more detail by the following examples.

#### Examples

The following substances were used:

A1) Tall oil fatty acid containing as main components 30% oleic acid, 60% linoleic acid and other polyunsaturated fatty acids, and 4% saturated fatty acids. Iodine number 155 g I/100 g.

A2) Oleic acid (technical grade) containing as primary components 69% oleic acid, 12% linoleic acid, 5% hexadecenoic acid and 10% saturated fatty acids. Iodine number 90 g I/100 g.

B1) Reaction product of a terpolymer of C<sub>14/16</sub>  $\alpha$ -olefin, maleic anhydride and allyl polyglycol with 2 equivalents ditallow fatty amine, 50% in solvent naphtha.

B2) Reaction product of a dodecenylspirobis lactone with a mixture of primary and secondary tallow fatty amine, 60% in solvent naphtha.

B3) Nonylphenol-formaldehyde resin, 505 in solvent naphtha.

B4) Mixture of 2 parts B1 and 1 part B2.

B5) Amide-ammonium salt based on ethylenediaminetetraacetic acid with 3 equivalents ditallow fatty amine in accordance with EP 0597278.

B6) Mixture of amide-ammonium salt based on ethylenediaminetetraacetic acid with 4 equivalents ditallow fatty amine and copolymer of equal parts maleic anhydride and C<sub>20/24</sub> olefin, imidated with N-tallow fatty propylenediamine in accordance with EP-0 909 307.

B7) Amide-ammonium salt of 1 mol phthalic anhydride and 2 mol of a mixture of equal parts ditallow and dicoco fatty amine.

B8) Mixture of equal parts

a) Amide-ammonium salt of 1 mol phthalic anhydride and 2 mol ditallow fatty amine and

b) Copolymer of fumaric acid di(tetradecyl ester), 50% in solvent naphtha.

To evaluate the low-temperature properties the pour point (ISO 3016, Table 1) and the cloud point (ISO 3015, Table 2) of the mixtures in accordance with the invention were measured.

Then the additive mixtures in accordance with the invention were stored for several days at various temperatures and visually evaluated (Tables 3 to 5). "V" indicates comparison examples.

Table 1. Pour points of additives in accordance with the invention

		② Zusammensetzung (Gew.-Teile)						Pour Point
①	Beispiel	A1	A2	B1	B2	B3	B4	
	1	80		20				-9
	2	50		50				-24
	3	20		80				0
	4	80			20			-9
	5	50			50			-24

[Table 1, continued]

	(2)	Zusammensetzung (Gew.-Telle)					Pour Point
6	20			80			-6
7	80				20		0
8	50				50		-15
9	20				80		-48
10	80					20	-9
11	50					50	-18
12	20					80	-15
13		80	20				-27
14		50	50				-27
15		20	80				-6
16		80		20			-27
17		50		50			-54
18		20		80			-45
19		80			20		-21
20		50			50		-30
21		20			80		-21
22		80				20	-21
23		50				50	-21
24		20				80	-9
25*	99,95		0,05				-38
26*	99,95					0,05	-36
27	99,95		0,05				-15
V1	100						-9
V2		100					6
V3			100				9
V4				100			-12
V5					100		0
V6						100	-6
V7*	100						-38

\* These examples are obtained with a 50% standardization of the fatty acid in solvent naphtha.

Key: 1 Example  
2 Composition (parts by weight)

Table 2. Cloud points of additives in accordance with the invention

	(2) Zusammensetzung (Gew.-Teile)						Cloud Point
(1) Beispiel	A1	A2	B1	B2	B3	B4	
V8*	100						-27,0
28*	99,9995		0,0005				-33,0
29*	99,9995					0,0005	-30,5
30*	99,998		0,002				-33,5
31*	99,998					0,002	-33,5
32*	99,995		0,005				-31,0
33*	99,995					0,005	-32,2
34** (B5)	99,998		0,002				-29,0
35** (B6)	99,998		0,002				-31,0
36** (B7)	99,998		0,002				-35,5
37** (B8)	99,998		0,002				-37,0

\* These examples are obtained with a 50% standardization of the fatty acid in solvent naphtha.

\*\* These examples refer to mixtures of A1 with 2000 ppm each B5 through B8, and were obtained with a 50 wt% standardization of the fatty acid in solvent naphtha.

Key: 1 Example  
2 Composition (parts by weight)

Table 3. Storage stability of the additives (3 days storage at -20°C)

Beispiel (1)	Zusammensetzung (Gew.-Teile) <sup>(2)</sup>				Beurteilung (3)
	A2	B1	B2	B3	
38	50	50			viskos (4)
39	80		20		flüssig
40	20		80		flüssig (5)
41	50			50	flüssig
42	20			80	flüssig

(1) Beispiel	Zusammensetzung (Gew.-Teile) <sup>(2)</sup>				Beurteilung (3)
V9	100				fest, wachsig (6)
V10		100			fest (7)
V11			100		fest
V12				100	viskos (4)

- Key:
- 1 Example
  - 2 Composition (parts by weight)
  - 3 Evaluation
  - 4 Viscose
  - 5 Liquid
  - 6 Solid, waxy
  - 7 Solid

Table 4. Storage ability of the additives in accordance with the invention dissolved in solvents at -20°C unless otherwise indicated

1	2		3	4					5
	Bestandteil A	Bestandteil B		nach 1 Tag	nach 3 Tagen	nach 5 Tagen	nach 7 Tagen	danach 1 Tag bei -28 °C	
V13	A1 (50 % in S.N.)	ohne Zusatz		Klar, Sediment (kristallin) 7	Klar, Sediment (kristallin) 7	Klar, Sediment (kristallin) 7	Klar, Sediment (kristallin) 7	Klar, Sediment (kristallin) 7	
43	"	B1	100	Klar, wenig Kristalle am Boden 8	Klar, wenig Kristalle am Boden 8	Klar, wenig Kristalle am Boden 8	Klar, wenig Kristalle am Boden 8	Klar, Sediment (kristallin) 7	
44	"	"	500	Klar, kein Sediment 9	Klar, wenig Kristalle am Boden 8	Klar, wenig Kristalle am Boden 8	Klar, wenig Kristalle am Boden 8	Klar, Sediment (kristallin) 7	
45	"	"	1.000	Klar, kein Sediment 9	Klar, kein Sediment 9	Klar, kein Sediment 9	Klar, kein Sediment 9	Klar, Sediment (kristallin) 7	
46	"	"	5.000	Klar, kein Sediment 9	Klar, kein Sediment 9	Klar, kein Sediment 9	Klar, kein Sediment 9	Klar, kein Sediment 9	
47	"	"	10.000	Klar, kein Sediment 9	Klar, kein Sediment 9	Klar, kein Sediment 9	Klar, kein Sediment 9	Klar, kein Sediment 9	
48	"	"	50.000	trüb, kein Sediment 10	trüb, kein Sediment 10	trüb, kein Sediment 10	trüb, kein Sediment 10	trüb, kein Sediment 10	
49	"	B4	100	Klar, wenig Kristalle am Boden 8	Klar, wenig Kristalle am Boden 8	Klar, wenig Kristalle am Boden 8	Klar, wenig Kristalle am Boden 8	Klar, Sediment (kristallin) 7	
50	"	"	500	Klar, kein Sediment 9	Klar, kein Sediment 9	Klar, wenig Kristalle am Boden 8	Klar, wenig Kristalle am Boden 8	Klar, Sediment (kristallin) 7	
51	"	"	1.000	Klar, kein Sediment 9	Klar, kein Sediment 9	Klar, kein Sediment 9	Klar, kein Sediment 9	Klar, kein Sediment 9	
52	"	"	5.000	Klar, kein Sediment 9	Klar, kein Sediment 9	Klar, kein Sediment 9	Klar, kein Sediment 9	Klar, kein Sediment 9	
53	"	"	10.000	Klar, kein Sediment 9	Klar, kein Sediment 9	Klar, kein Sediment 9	Klar, kein Sediment 9	Klar, kein Sediment 9	
54	"	"	50.000	Klar, kein Sediment 9	Klar, kein Sediment 9	Klar, kein Sediment 9	Klar, kein Sediment 9	leicht trüb, kein Sediment 11	
55	"	B3	5.000	Klar, kristalline Ausfällungen in der Schwebphase	Klar, kristalline Ausfällungen in der Schwebphase	Klar, kristalline Ausfällungen in der Schwebphase	Klar, kristalline Ausfällungen in der Schwebphase	trüb, kristalline Ausfällungen in der Schwebphase	

S.N. = Solvent Naphtha

Key: 1 Example  
2 Component \_\_\_\_  
3 Amount, ppm  
4 After \_\_\_\_ day or days  
5 Then 1 day at -28°C  
6 Without additives  
7 Clear, sediment (crystalline)  
8 Clear, few crystals on bottom  
9 Clear, no sediment  
10 Cloudy, no sediment  
11 Slightly cloudy, no sediment  
12 Clear, crystalline precipitates in suspension



Table 5. Storage stability of the additives in accordance with the invention dissolved in solvents at -20°C unless otherwise indicated

Beispiel (1)	Bestandteil A (2)	Bestandteil B (2)	Menge (3) ppm	(4)		
				nach 3 Tagen	nach 7 Tagen	darauf 1 Tag bei -28 °C (5)
V14	A1 (50 % in MS)	ohne Zusatz		klar, Sediment (kristallin) (7)	klar, Sediment (kristallin) (7)	klar, Sediment (kristallin), fest (8)
55	"	(6) B1	1.000	klar, kein Sediment (9)	klar, kein Sediment (9)	trüb, Sediment (10)
57	"	"	5.000	trüb, kein Sediment (11)	trüb, kein Sediment (11)	trüb, kein Sediment (11)
58	"	"	10.000	trüb, kein Sediment (11)	trüb, kein Sediment (11)	trüb, kein Sediment (11)
59	"	B4	1.000	klar, kein Sediment (9)	klar, wenig Sediment (12)	leicht trüb, Sediment (13)
60	"	"	5.000	klar, kein Sediment (9)	klar, kein Sediment (9)	trüb, kein Sediment (11)
61	"	"	10.000	klar, leichte Trübung am Boden, kein Sediment (14)	trüb, kein Sediment (11)	trüb, kein Sediment (11)
62	"	"	50.000	trüb, kein Sediment (11)	trüb, kein Sediment (11)	trüb, kein Sediment (11)

Key:	1	Example
	2	Component ____
	3	Amount, ppm
	4	After ____ day or days
	5	Then 1 day at -28°C
	6	Without additives
	7	Clear, sediment (crystalline)
	8	Clear, sediment (crystalline). solid
	9	Clear, no sediment
	10	Cloudy, sediment
	11	Cloudy, no sediment
	12	Clear, a little sediment
	13	Slightly cloudy, sediment
	14	Clear, slightly cloudy at bottom, no sediment

MS is a mixture of a series of aliphatic and cyclic nonaromatic hydrocarbons. The primary components can be taken from the following table:

Table 6. Components of MS

Component	Concentration range (wt%)
Di-2-ethylhexyl ether	10-25
2-Ethylhexyl 2-ethylhexanoate	10-25
C <sub>16</sub> Lactones	4-20
2-Ethylhexyl butyrate	3-10
2-Ethylhexane-(1,3)-diol mono-n-butyrate	5-15
2-Ethylhexanol	4-10
C <sub>4</sub> to C <sub>8</sub> Acetates	2-10
2-Ethylhexanes-1,3-diol	2-5
Ethers and Esters $\geq$ C <sub>20</sub>	0-20

#### Lubricant Effect in Middle Distillates

The lubricant effect of the additives was conducted [sic; tested] on treated oils at 60°C using an HFRR instrument of the company PCS Instruments. The High Frequency Reciprocating Rig test (HFRR) is described in D. Wei, H. Spikes, Wear, Vol. 111, No. 2, p. 217, 1986. The results are given as coefficient of friction and wear scar (WS1.4). A low coefficient of friction and low wear scar show good lubricating effect.

Table 7. Characterization of Test Oils

Test oils with the following characteristics were used for testing the lubricating effect:

	Testöl 1 (1)	(1) Testöl 2
Siedebereich: (2)	170 - 344°C	182-304°C
Dichte (3)	0,830 g/cm³	0,821 g/cm³
Cloud Point	-9°C	-33°C
Schwefelgehalt (4)	45 ppm	6 ppm

Key: 1 Test oil  
 2 Boiling range  
 3 Density  
 4 Sulfur content

The boiling range data are determined in accordance with ASTM D-86 and the cloud point is determined in accordance with ISO 3015.

Table 8. Wear Scar in Test Oil 1

(1) Beispiel	Additiv (2)	Wear Scar	Friction
V15	Ohne (3)	555 µm	0,33
63	100 ppm gemäß Bsp. 37 (4)	385 µm	0,18
64	100 ppm A1+ 150 ppm B4	381 µm	0,18
V16	100 ppm A1	421 µm	0,18
V17	150 ppm B4	549 µm	0,34

Key: 1 Example  
 2 Additive  
 3 None  
 4 100 ppm in accordance with Example 37

Table 9. Wear Scar in Test Oil 2

<sup>①</sup> Beispiel	Additiv <sup>②</sup>	Wear Scar	Friction
V18	ohne <sup>③</sup>	637 $\mu$ m	0,30
65	200 ppm gemäß Bsp. 42 <sup>④</sup>	386	0,18
66	200 ppm gemäß Bsp. 48 <sup>⑤</sup>	395	0,18
V19	200 ppm gemäß Bsp. V13 <sup>⑥</sup>	405	0,19

Key: 1 Example  
 2 Additive  
 3 None  
 4 200 ppm in accordance with Example 42  
 5 200 ppm in accordance with Example 48  
 6 200 ppm in accordance with Example V13

Claims

1. Low-temperature stabilized additives for fuel oils that contain up to 0.05 wt% sulfur, containing fatty acid mixtures of

A1) 1 to 99 wt% of at least one saturated mono- or dicarboxylic acid with 6 to 50 carbon atoms,

A2) 1 to 99 wt% of at least one unsaturated mono- or dicarboxylic acid with 6 to 50 carbon atoms,

and

B) At least one polar nitrogen-containing compound that is active as a paraffin disperser in middle distillates, in an amount from 0.1 to 90 wt% with respect to the total weight of A1, A2 and B.

2. Additives as in Claim 1, in which component A consists of carboxylic acids with 12 to 22 carbon atoms.

3. Additives as in Claim 1 and/or 2, containing 1 to under 20 wt% A1 and over 80 to 99 wt% A2.

4. Additives as in one or more of Claims 1 to 3 in which the mixture of A1 and A2 has an iodine number of at least 40 g I/100 g.

5. Additives as in one or more of Claims 1 to 4 in which the mixture of A1 and A2 consists of 1 to 40 wt% resin acids.

6. Additives as in one or more of Claims 1 to 5, in which oil-soluble polar amine salts or amides are contained as paraffin dispersers.

7. Low temperature stabilized solutions of additives as in one or more of Claims 1 to 6 in organic solvents, where the solutions contain 1 to 80 wt%.

8. Low temperature stabilized solutions as in Claim 7, where aliphatic and/or aromatic and/or oxygen-containing hydrocarbons are used as solvents.

9. Low temperature stabilized fatty acid mixtures containing

A1) 1 to 99 wt% of at least one saturated mono- or dicarboxylic acid with 6 to 50 carbon atoms,

A2) 1 to 99 wt% of at least one unsaturated mono- or dicarboxylic acid with 6 to 50 carbon atoms,

and

B) At least one polar nitrogen-containing compound that is active as a paraffin disperser in middle distillates, in an amount from 0.1 to 90 wt% with respect to the total weight of A1, A2 and B.

10. Fuel oils containing, in addition to a middle distillate that contains up to 0.05 wt% sulfur, an additive as in one or more of Claims 1 to 9.

11. The use of additives as in one or more of Claims 1 to 9 to improve the lubricating properties of low-sulfur middle distillates that contain up to 0.05 wt% sulfur.

#### Abstract

Fuel oil with improved lubricant effect containing mixtures of fatty acids with paraffin dispersers, and a lubricant-improving additive.

The object of the invention consists of low temperature stabilized additives for fuel oils that contain up to 0.05 wt% sulfur, which contain fatty acid mixtures of

A1) 1 to 99 wt% of at least one saturated mono- or dicarboxylic acid with 6 to 50 carbon atoms,

A2) 1 to 99 wt% of at least one unsaturated mono- or dicarboxylic acid with 6 to 50 carbon atoms,

and

B) At least one polar nitrogen-containing compound that is active as a paraffin disperser in middle distillates, in an amount from 0.1 to 90 wt% with respect to the total weight of A1, A2 and B.

and the use of the said mixtures to improve the lubricating properties of low-sulfur middle distillates.

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